

Reversible assembly of silver nanoparticles driven by host–guest interactions based on water-soluble pillar[*n*]arenes

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1. Materials and methods

The water-soluble pillar[5]arene **WP5**, water-soluble pillar[6]arene **WP6**, and guest molecules **G** were prepared according to the method previously reported.^{S1, S2, S3} The TEM images were obtained using a JEM-1200EX instrument with an accelerating voltage of 80 kV. UV–Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV–Vis spectrometer. The fluorescence titration experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

2. Synthesis of **WP5**-stabilized silver nanoparticles

WP5-stabilized silver nanoparticles were synthesized by the reduction of AgNO₃ in the presence of **WP5**. In a typical synthesis, AgNO₃ (20.0 μ L, 10.0 mM) was added to deionized water (20.0 mL), followed by the addition of an aqueous solution of **WP5** (1.00 mL, 0.100 mM). NaBH₄ (20.0 μ L, 0.100 M) was freshly prepared with deionized ice water and added to the above reaction mixture while stirring. The solution immediately turned yellow and **WP5**-stabilized silver nanoparticles were thus obtained. This concentration of **WP5**-stabilized silver nanoparticles was used in all experiments unless otherwise noted.

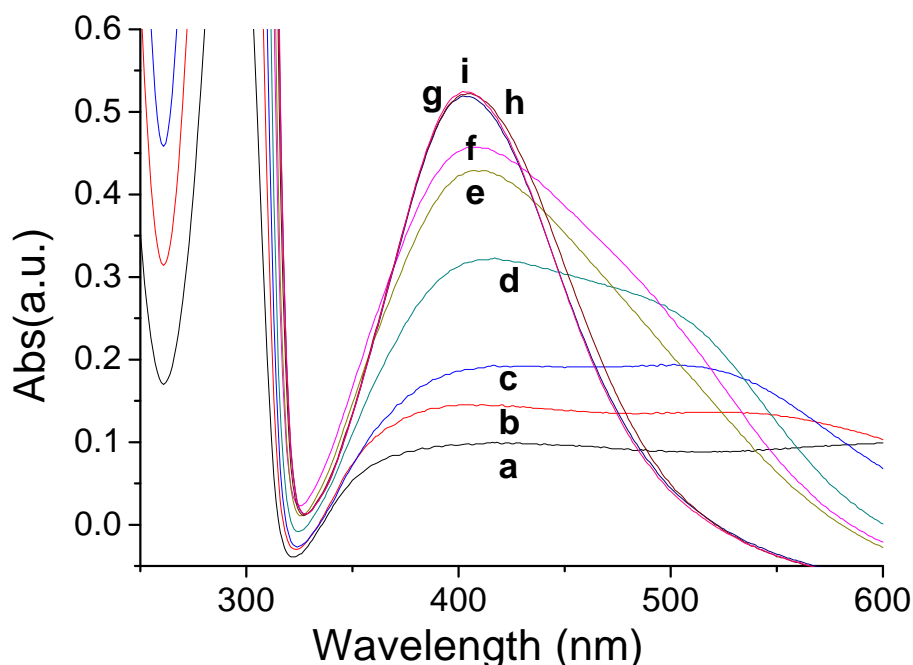


Fig. S1. UV–Vis spectra of silver nanoparticles with different concentrations of **WP5** as stabilizer: (a) 2.00×10^{-5} M; (b) 5.00×10^{-5} M; (c) 1.00×10^{-4} M; (d) 1.50×10^{-4} M; (e) 2.00×10^{-4} M; (f) 3.00×10^{-4} M; (g) 4.00×10^{-4} M; (h) 6.00×10^{-4} M; (i) 8.00×10^{-4} M.

3. Assembly of **WP5**-stabilized AgNPs by addition of **G**.

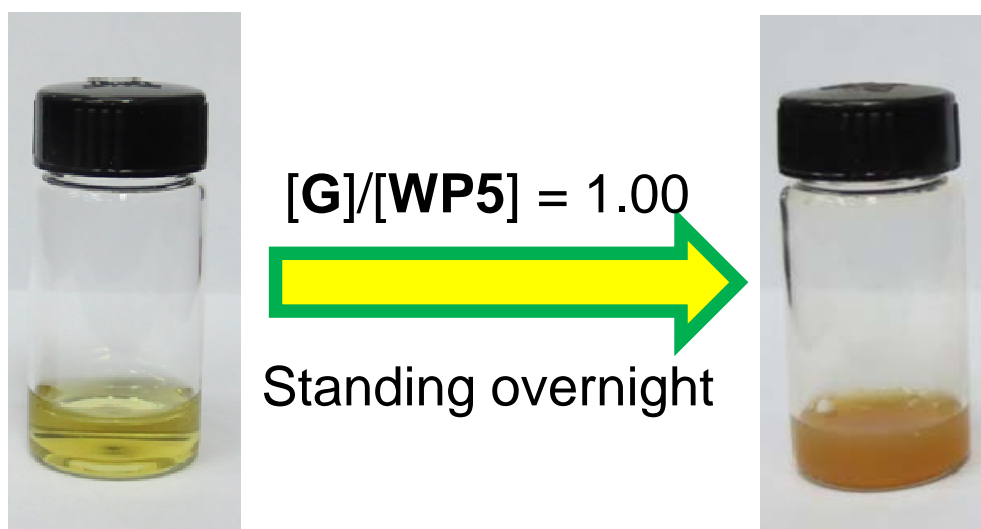


Fig. S2. Optical pictures of **WP5**-stabilized silver nanoparticles and after addition of **G**. $[G]/[WP5] = 1.00$.

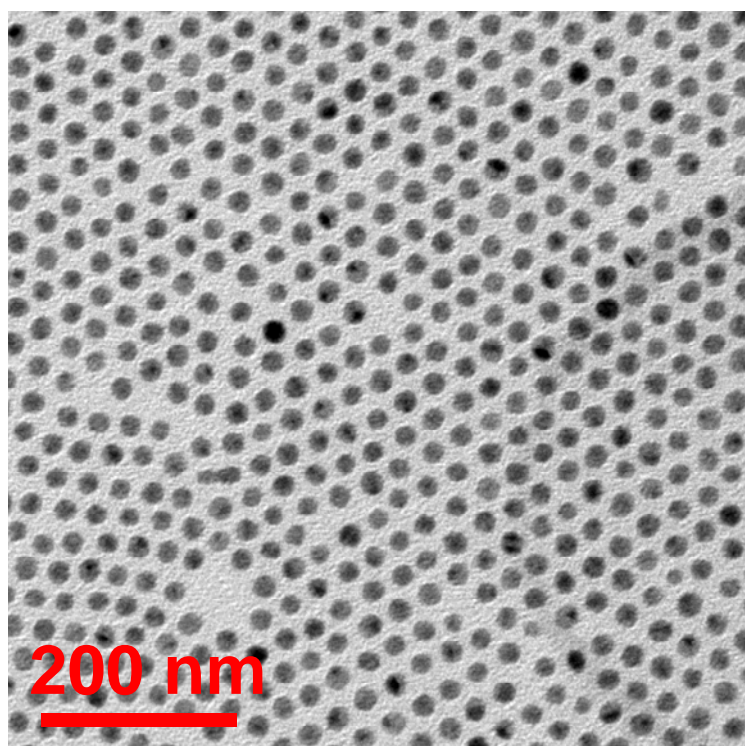


Fig. S3. TEM image of **WP5**-stabilized silver nanoparticles without **G**.

4. Disassembly of silver assemblies by addition of **WP6**.

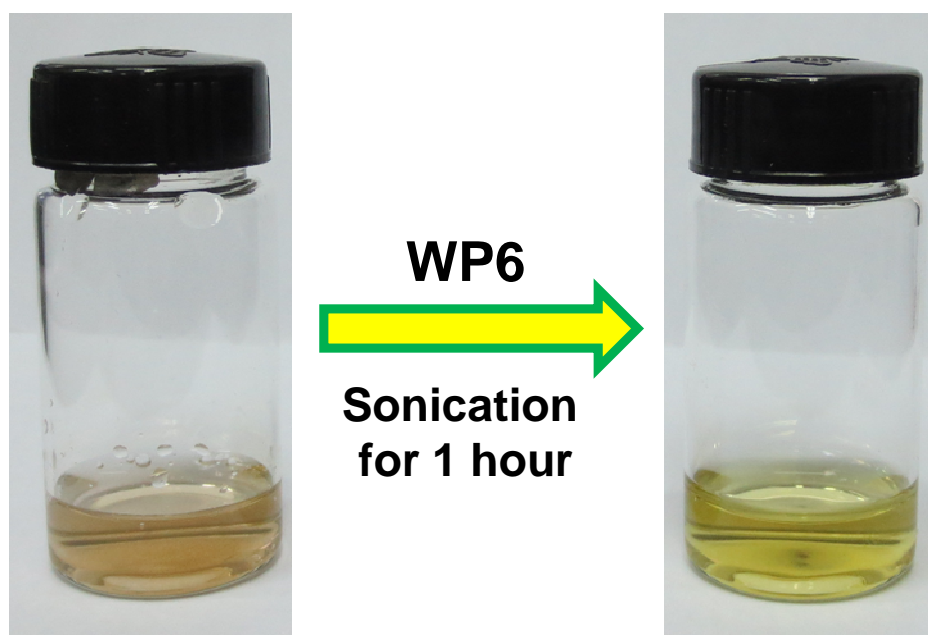


Fig. S4. Optical pictures of silver assemblies and after addition of excess **WP6**.

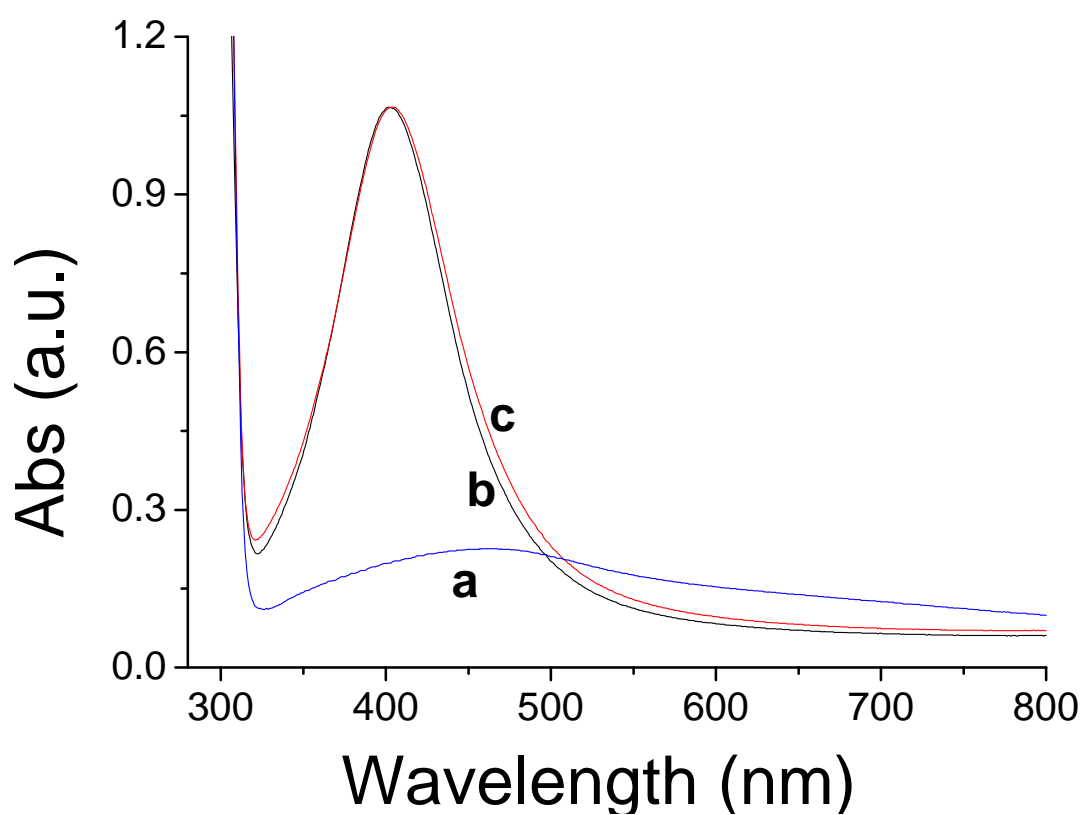


Fig. S5. UV–Vis spectra: (a) silver assemblies; (b) addition of excess **WP6** and sonication for 1 hour; (c) addition of excess **WP6** and sonication for 8 hour.

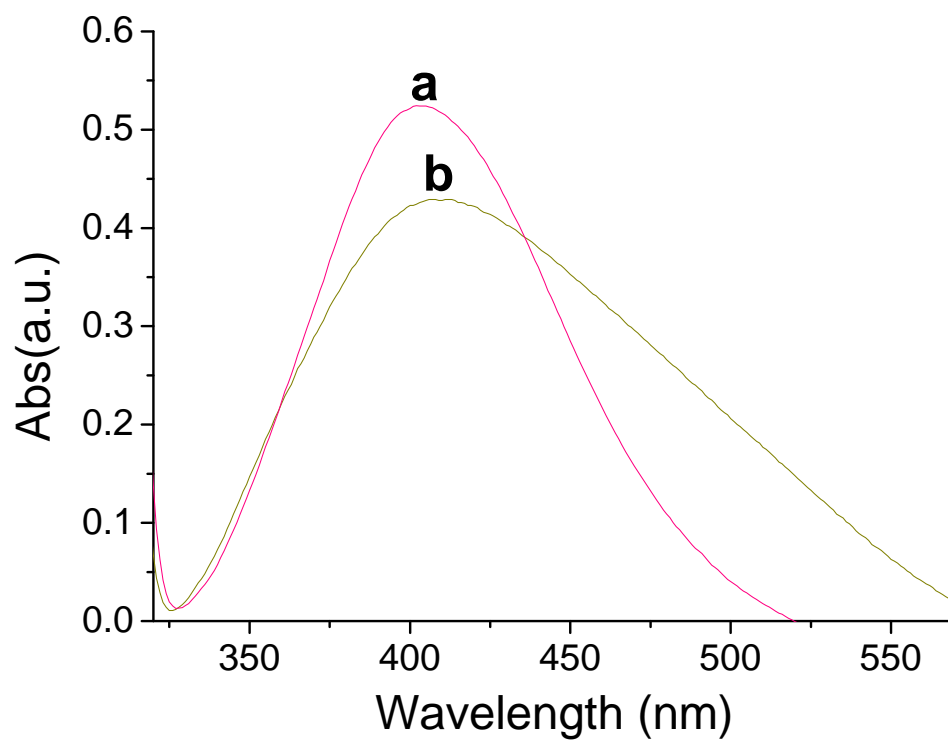


Fig. S6. UV–Vis spectra of silver nanoparticles: (a) after addition of excess **WP6** and sonication for 1 hour; (b) after centrifugation and subsequent immediate redispersion in water.

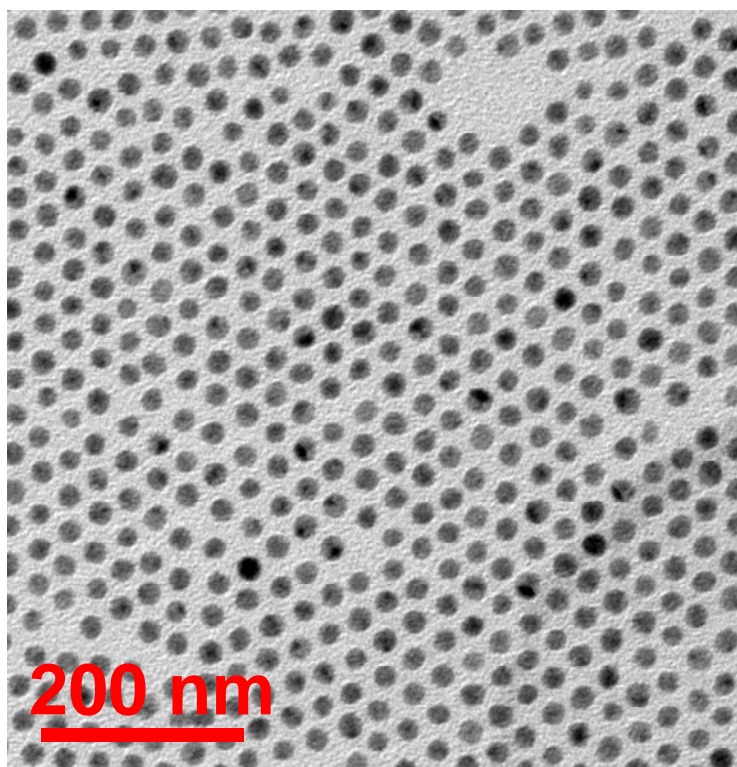


Fig. S7. TEM image of the redispersed **WP5** stabilized silver nanoparticles.

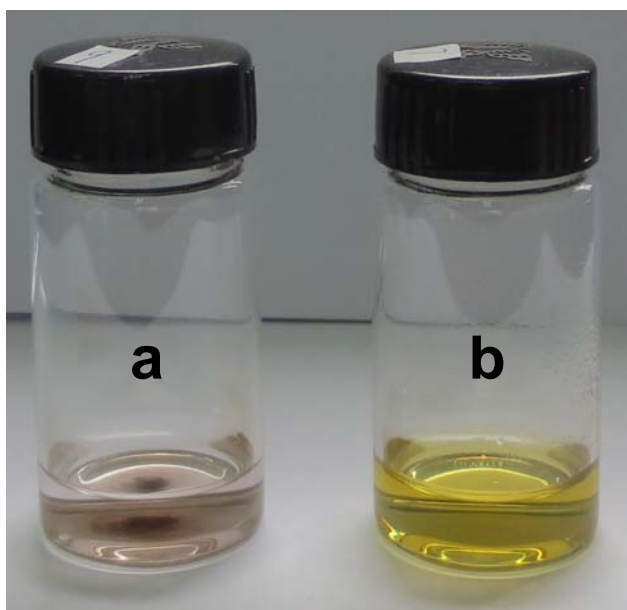


Fig. S8. Optical pictures: (a) silver assemble solution when $[G]/[WP5]$ was as high as 10.0; (b) after addition of excess **WP6** and sonication for 1 hour.

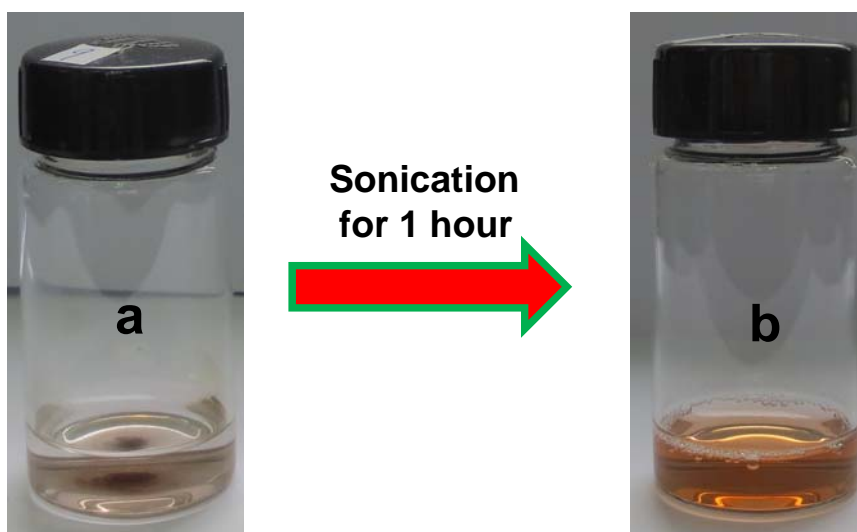


Fig. S9. Optical pictures: (a) silver assemble solution when $[G]/[WP5]$ was as high as 10.0; (b) after sonication for 1 hour.

5. References:

- S1. (a) T. Ogoshi, M. Hashizume, T. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2010, **46**, 3708; (b) Y. Yao, Y. Zhou, J. Dai, S. Yue and M. Xue, *Chem. Commun.*, 2014, **50**, 869.
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- S3. H. Li, D.-X. Chen, Y.-L. Sun, Y. B. Zheng, L.-L. Tan, P. S. Weiss and Y.-W. Yang, *J. Am. Chem. Soc.*, 2013, **135**, 1570.